

New possibilities of recently constructed high-temperature solution calorimeter

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Abstract The calorimeter presented in this paper is constructed under supervision of authors. The most substantial innovation of construction of the device was introduction of intermediate container with ten sockets. As a result the calorimeter is used for determination of enthalpy of formation for alloys in a wide range of temperature (up to 1,400 K). As an example results from alloys from the Ni–Al–Cr system are presented, they are aimed to determine directly $\gamma' / \gamma' + \gamma / \gamma$ phase boundaries with use of this “in situ” calorimetric method. Precise indication of phase boundaries is crucial for determination of phase diagrams.

Keywords Solution calorimetry · Enthalpy of formation · Intermetallic phase · Phase boundary

Introduction

High-temperature calorimetry solution type is a very precise method for examining of reactions occurring in solids and liquids. This measurement technique enables solving problems connected with explaining phenomena in metals, alloys, ions of metals of different oxidation state or during order–disorder transition.

Calorimetric measurement allows direct determination of molar enthalpy of formation, that is one of the most important thermodynamic data used in computing and

phase diagrams optimization. Calorimetry used for determination of enthalpy of formation, uses two measurement methods: direct and indirect, in this case (calorimetry solution type) indirect method is performed. For binary alloys, value of enthalpy of formation results from the difference between heat effects accompanying solving separately of components and alloy in the bath. It is worth mentioning that the alloy obtained before the calorimetric experiment and its components are dissolved in the same type of solvent.

In typical high-temperature solution calorimeters, examined sample is dropped into calorimeter from room temperature. Thermal effect observed presents change of temperature of the bath. Two-stage method of sample dropping is performed. At first, alloy examined is kept in elevated temperature; next after reaching thermal balance, sample is dropped into the solvent.

Therefore, authors of the paper decided to construct high-temperature calorimeter solution type. It was modified and the most crucial innovation was introducing indirect container with ten sockets. This improvement allows to determine enthalpy of formation in a wide range of temperatures (up to 1,400 K). The other construction changes are supposed to enable access to interior of the furnace, heating system structure, and shielding gas dosing system.

Thermodynamic data resulting from measurement and calorimetric research are necessary for phase diagrams optimization. All data is collected in databases such as CALculations of PHase Diagrams (CALPHAD) and are used also for prediction of phase transitions.

In metallurgical research, precise knowledge about thermodynamic properties of alloys is of great importance. Changes in enthalpy of formation values reflect changes in alloy structure and its properties. As an example of using high-temperature calorimeter solution type, alloy research

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based on intermetallic phase Ni_3Al from Ni–Al–Cr system was presented. Alloys from this system are in the center of interest of scientific society and industry [1–7]. Thanks to specific properties, they can be applied for work in elevated temperatures. In this paper alloys from $\text{Ni}_{75}\text{Al}_{25}$ – $\text{Ni}_{75}\text{Cr}_{25}$ system in three different temperatures were examined: 873, 996, and 1,150 K. Authors suggested new approach in calorimetric technique, that is direct determination of phase boundaries on basis of course of changes of formation enthalpy values of those alloys.

Device construction

Construction of high-temperature solution calorimeter

Appearance of calorimetric stand is presented on Fig. 1. The main part of the device is vertical barrel-shaped furnace, located in the lower part of calorimeter. The furnace is heated with three independent heat windings. Windings are made of kanthal tape wound on ceramic pipe, inside which heat-resistant container with calorimetric block is placed. Construction change is application of three windings of different length, the middle winding and upper one are of the same length, and lower winding is longer. It allowed to lengthen area of constant temperature. Crucible with metallic bath is located in lower winding zone. Every winding is supplied independently and controlled by separate controllers; as a result, thermal gradient in vertical axis of furnace is kept. Controllers allow to keep temperature with 0.1 °C accuracy.

Inside the furnace is located heat-resistant container with calorimetric block and in higher part it is connected with calorimeter head. The head is divided into three parts: upper, middle, and lower (Fig. 2). After disconnecting of middle and lower part, calorimetric block can be raised. Block is mounted on heat-resisting steel rods. It enables to exchange metallic bath or any other operations performed between experimental series. Construction of device also allows to eject whole heat-resisting container with ceramic pipe and calorimetric block. This is necessary action in case of repair work of changing of heat windings of the furnace.

Head of calorimeter is connected directly with sample dosing system and with a stirrer of regulated rotation speed drive. Through the head pass thermocouple outlet and thermocouple stack also argon inlet and outlet that is responsible for inert atmosphere during experiment.

Upper part of sample dosing system are two quartz locks. One doses samples directly into the bath, and the second one is for placing samples in intermediate container. In both locks atmosphere is purified with argon during placing samples in a lock. It was possible to obtain



Fig. 1 Appearance of calorimetric stand

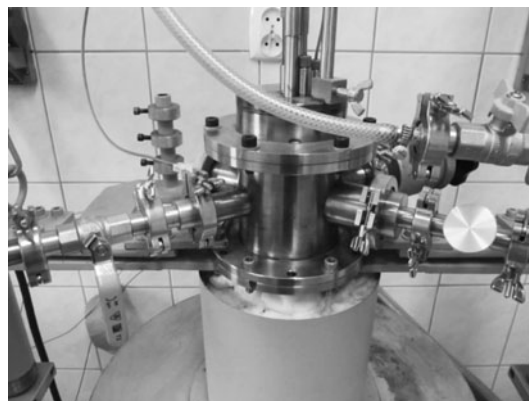


Fig. 2 Calorimeter head

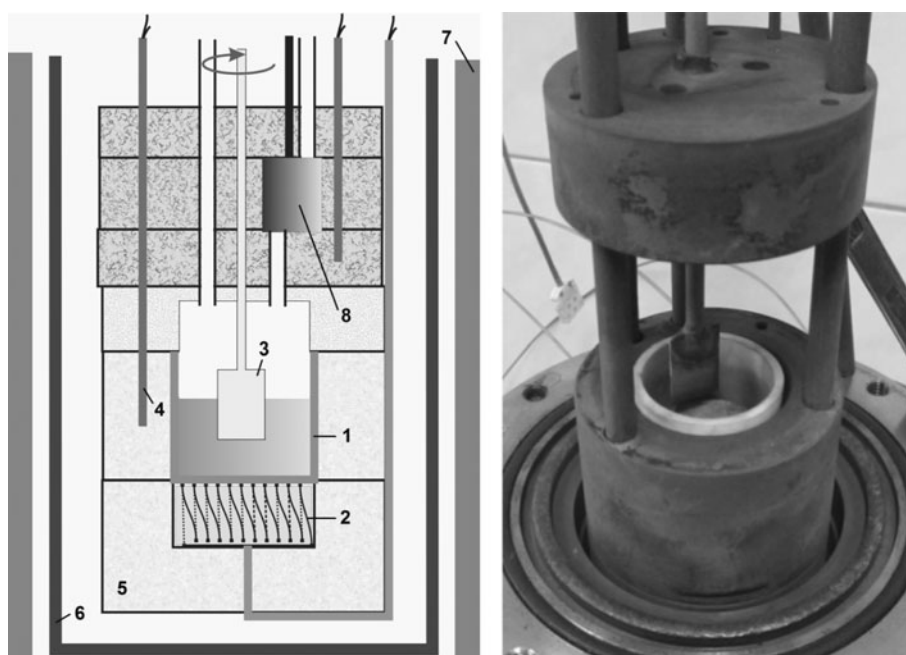
by applying valve system and connection with vacuum pump set (rotary and turbo molecular).

Calorimetric block

Calorimetric block is the most important part of the device. It is placed inside of calorimeter. Scheme of calorimetric block and its outlook after withdrawal and partial assembly shows Fig. 3.

On the scheme presented on Fig. 3 alundum crucible (1) which has internal diameter around 35 mm and can contain aluminum bath of 50 g mass is shown. Mass of samples is 0.1–0.8 g that is minimal fraction of bath mass. Small

Fig. 3 On the left is calorimetric block scheme and on the right is calorimetric block withdrawn from furnace and with separated body elements



change of degree of fulfillment of crucible during experiment is extremely crucial in calorimetric experiment. Directly under crucible bottom is presented thermopile (2) consisting of around forty series connected to each other thermocouples K type (NiAl–NiCr). It was used for measuring thermal effect accompanying dropping the sample into the bath. Alundum stirrer (3) is also presented in the Fig. 3. It results in obtaining a homogeneous composition of bath bulk, and accuracy of measurement is increased. Temperature of calorimetric block is measured with thermocouple K type (4). Main body of calorimetric block (5) shown in the Fig. 3 is made of heat-resisting steel. It is placed in heat-resisting steel container (6), this part is

located inside calorimeter furnace (7) and is characterized by significant thermal inertia.

Very important change in construction was introducing intermediate container (8). Its use is necessary when determination of set of thermodynamic function is the aim, simultaneously having Gibbs energy, in defined elevated temperature, or necessity of prolonged heating of samples occur in order to reach thermodynamic balance. Intermediate container can be heated up to 1,400 K thanks to using few independent heat windings and also thanks to possibility to place it in any height of furnace. Container has mechanism allowing its rotation (Fig. 4) and it consists of 11 sockets, that allows to heat 10 samples simultaneously.

Fig. 4 On the left is intermediate container and on the right is container rotation mechanism



Table 1 Enthalpy of formation for alloys from Ni₇₅Al₂₅–Ni₇₅Cr₂₅ pseudo-binary at 873 K

Alloy	Temperature/K	Measurement no.	Enthalpy of formation $\Delta_f H$ /kJ mole of atoms ⁻¹
Ni _{75.0} Al _{25.0} ^a	873	Average	–42.0
		Standard Dev.	1.4
Ni _{75.0} Al _{23.0} Cr _{2.0} ^a	873	Average	–39.0
		Standard Dev.	1.6
Ni _{75.0} Al _{21.0} Cr _{4.0} ^a	873	Average	–39.8
		Standard Dev.	1.7
Ni _{75.0} Al _{18.5} Cr _{6.5} ^a	873	Average	–37.3
		Standard Dev.	2.4
Ni _{75.0} Al _{16.0} Cr _{9.0} ^a	873	Average	–32.0
		Standard Dev.	2.4
Ni _{75.0} Al _{13.5} Cr _{11.5} ^a	873	Average	–24.2
		Standard Dev.	2.5
Ni _{75.0} Al _{11.0} Cr _{14.0} ^a	873	Average	–20.1
		Standard Dev.	2.3
Ni _{74.9} Al _{8.1} Cr _{17.0}	873	1	–17.7
		2	–13.8
		3	–14.6
		Average	–15.4
		Standard Dev.	2.1
Ni _{75.1} Al _{6.1} Cr _{18.8}	873	1	–13.3
		2	–10.5
		3	–11.9
		Average	–11.9
		Standard Dev.	1.4
Ni _{75.0} Al _{5.1} Cr _{19.9}	873	1	–6.7
		2	–8.2
		3	–7.4
		Average	–7.4
		Standard Dev.	0.8
Ni _{75.0} Al _{3.7} Cr _{21.3}	873	1	–8.9
		2	–9.8
		3	–5.8
		Average	–8.2
		Standard Dev.	2.1
Ni _{75.1} Al _{1.6} Cr _{23.3}	873	1	–7.1
		2	–7.4
		3	–6.9
		Average	–7.1
		Standard Dev.	0.6

^a Data from [9]

One of the sockets is used for dosing samples into metallic bath. For temperature measurement in indirect container thermocouple K type is used. Multi socket container limits measuring errors in experiment as well as it shortens substantially the time of carrying the experiment.

Measurement principle

Measurement principle of thermal effects in this “in situ” solution method is change of the temperature of bath, into which sample is dropped. Base temperature (temperature of

Table 2 Enthalpy of formation for alloys from Ni₇₅Al₂₅–Ni₇₅Cr₂₅ pseudo-binary at 996 K

Alloy	Temperature/K	Measurement no.	Enthalpy of formation $\Delta_f H$ /kJ mole of atoms ⁻¹
Ni _{75.0} Al _{25.0}	996	1	–41.5
		2	–39.8
		3	–41.0
		4	–42.7
		Average	–41.8
		Standard Dev.	0.9
Ni _{75.0} Al _{23.2} Cr _{1.8}	996	1	–41.0
		2	–39.7
		3	–37.8
		4	–38.7
		Average	–39.9
		Standard Dev.	1.1
Ni _{75.0} Al _{21.5} Cr _{3.5}	996	1	–40.1
		2	–37.5
		3	–37.8
		Average	–38.5
		Standard Dev.	1.4
Ni _{75.0} Al _{19.5} Cr _{5.5}	996	1	–34.4
		2	–36.3
		3	–31.9
		4	–35.0
		5	–34.0
		Average	–34.3
Ni _{75.0} Al _{17.7} Cr _{7.3}	996	1	–30.1
		2	–29.9
		3	–32.9
		Average	–31.0
		Standard Dev.	1.7
Ni _{75.0} Al _{15.9} Cr _{9.1}	996	1	–29.3
		2	27.1
		3	25.9
		Average	–27.4
		Standard Dev.	1.7
Ni _{75.0} Al _{14.2} Cr _{10.8}	996	1	–25.8
		2	–22.9
		3	–23.5
		Average	–24.1
		Standard Dev.	1.5
Ni _{75.0} Al _{11.8} Cr _{13.2}	996	1	–19.1
		2	–17.9
		3	–16.0
		4	–18.1
		Average	–17.8
		Standard Dev.	1.3

Table 2 continued

Alloy	Temperature/K	Measurement no.	Enthalpy of formation $\Delta_f H$ /kJ mole of atoms ⁻¹
Ni _{75.0} Al _{9.7} Cr _{15.3}	996	1	-12.7
		2	-14.3
		3	-14.2
		4	-15.7
		Average	-14.2
		Standard Dev.	1.2
Ni _{74.9} Al _{8.1} Cr ₁₇	996	1	-11.3
		2	-7.4
		3	-10.6
		Average	-9.8
		Standard Dev.	2.1
Ni _{75.1} Al _{6.1} Cr _{18.8}	996	1	-8.0
		2	-5.0
		3	-7.8
		Average	-6.9
		Standard Dev.	1.6
Ni _{75.0} Al _{5.1} Cr _{19.9}	996	1	-7.1
		2	-5.2
		3	-7.8
		Average	-6.7
		Standard Dev.	1.3
Ni _{75.0} Al _{3.7} Cr _{21.3}	996	1	-4.5
		2	-8.2
		3	-6.8
		Average	-6.5
		Standard Dev.	1.9

calorimetric block between single measurements) in one series of measurement remains stable. Determination of formation enthalpy with use of high-temperature solution calorimeter relies on comparison of heat effects accompanying dissolving of alloys and its components in metallic bath.

For ternary alloys it can be presented as:

$$\Delta_f H = x_A \Delta H_A^{\text{ef.}} + x_B \Delta H_B^{\text{ef.}} + x_C \Delta H_C^{\text{ef.}} - \Delta H_{A_{x_A} B_{x_B} C_{x_C}}^{\text{ef.}} \quad (1)$$

where $\Delta_f H$ —formation enthalpy of the alloy; x_A , x_B , x_C —concentrations (mole fractions) of the alloy components, $\Delta H_A^{\text{ef.}}$, $\Delta H_B^{\text{ef.}}$, $\Delta H_C^{\text{ef.}}$, $\Delta H_{A_{x_A} B_{x_B} C_{x_C}}^{\text{ef.}}$ —heat effects accompanying the dissolution of the components and the alloy in the bath. It is worth mentioning that thermal effect consists of: heating, melting, and solving of the sample in the bath. Enthalpy of formation is determined for temperature, from which sample is dropped into the bath.

Research

In this paper, alloys from Ni₇₅Al₂₅–Ni₇₅Cr₂₅ pseudo-binary were examined at three temperatures: 873, 996, and 1,150 K. With rise of Cr content, disordered phase γ begins to occur. Coexistence of the γ and γ' phases plays a significant role in controlling the mechanical properties of the material in elevated temperatures. It becomes crucial to know precisely course of phase boundaries $\gamma' / \gamma' + \gamma / \gamma$. Authors suggested a new approach to calorimetric technique that is direct determination of phase boundaries on basis of course of changes of formation enthalpies of alloys examined.

Alloys preparation

Alloys were prepared using casting method. Casting was performed in induction vacuum furnace VSG-02 Balzers, in alundum crucible in vacuum (10^{-2} torr). Alloys were

Table 3 Enthalpy of formation for alloys from Ni₇₅Al₂₅–Ni₇₅Cr₂₅ pseudo-binary at 1,150 K

Alloy	Temperature/K	Measurement no.	Enthalpy of formation $\Delta_f H$ /kJ mole of atoms ⁻¹
Ni _{75.0} Al _{25.0} ^a	1,150	Average	–42.3
		Standard Dev.	1.6
Ni _{75.0} Al _{23.0} Cr _{2.0} ^a	1,150	Average	–41.9
		Standard Dev.	1.4
Ni _{75.0} Al _{21.0} Cr _{4.0} ^a	1,150	Average	–38.3
		Standard Dev.	1.6
Ni _{75.0} Al _{18.5} Cr _{6.5} ^a	1,150	Average	–34.0
		Standard Dev.	1.9
Ni _{75.0} Al _{16.0} Cr _{9.0} ^a	1,150	Average	–25.8
		Standard Dev.	2.1
Ni _{75.0} Al _{13.5} Cr _{11.5} ^a	1,150	Average	–21.1
		Standard Dev.	2.6
Ni _{75.0} Al _{11.0} Cr _{14.0} ^a	1,150	Average	–14.5
		Standard Dev.	2.8
Ni _{75.0} Al _{9.5} Cr _{15.5} ^a	1,150	Average	–11.8
		Standard Dev.	2.9
Ni _{74.9} Al _{8.1} Cr _{17.0}	1,150	1	–11.2
		2	–8.5
		3	–9.5
		Average	–9.5
		Standard Dev.	1.4
Ni _{75.0} Al _{5.0} Cr _{20.0} ^a	1,150	Average	–9.5
		Standard Dev.	2.9
Ni _{75.0} Al _{3.7} Cr _{21.3}	1,150	1	–10.2
		2	–7.2
		3	–6.5
		Average	–7.9
		Standard Dev.	2.0
Ni _{75.1} Al _{1.6} Cr _{23.3}	1,150	1	–8.1
		2	–9.0
		3	–6.0
		Average	–7.7
		Standard Dev.	1.5

^a Data from [9]

casted into graphite form, rods of 3 mm diameter were obtained. The shape of samples is adequate to sample injection system in calorimeter. Chemical composition of the samples was analyzed. Dominant element in alloys, that is nickel was analyzed using gravimetric method; aluminum and chromium were analyzed with atomic absorption spectroscopy.

Experiment

Preparation of the experiment began with triple gas pumping out from the interior of calorimeter with use of turbo molecular pump, alternately argon of high purity

(99.9999 %) was introduced. Finally, experiments were conducted in argon atmosphere. Samples were placed in intermediate container and heated up to temperature required. Device was left for 24 h in order to stabilize base line and to achieve the equilibrium state of samples. Next, stirrer was installed, and device was ready for experiment. During first measurements of the series, the device was calibrated by dissolving aluminum samples; in this manner, amount of energy per conventional unit was determined [8]. After calibration, experimental samples were dropped into aluminum bath from intermediate container. Heat effect was registered by computer, a special software allowed to determine value of enthalpy accompanying

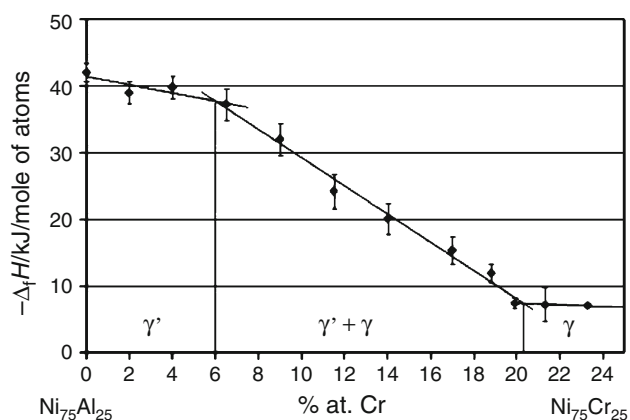


Fig. 5 Course of formation enthalpy of alloys from $\text{Ni}_{75}\text{Al}_{25}$ – $\text{Ni}_{75}\text{Cr}_{25}$ pseudo-binary as a function of chromium concentration at 873 K

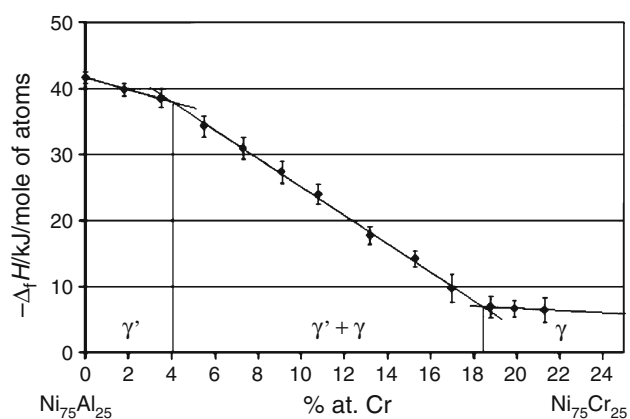


Fig. 6 Course of formation enthalpy of alloys from $\text{Ni}_{75}\text{Al}_{25}$ – $\text{Ni}_{75}\text{Cr}_{25}$ pseudo-binary as a function of chromium concentration at 996 K

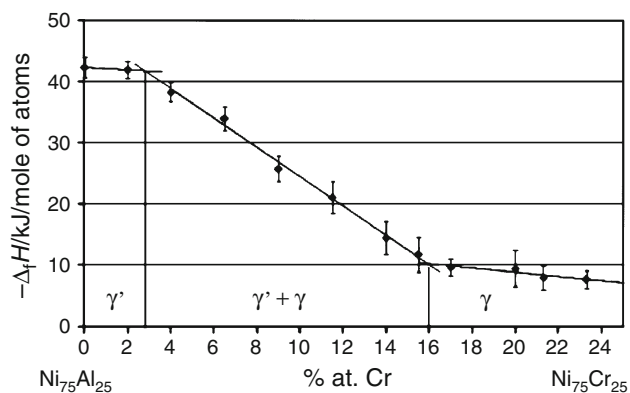


Fig. 7 Course of formation enthalpy of alloys from $\text{Ni}_{75}\text{Al}_{25}$ – $\text{Ni}_{75}\text{Cr}_{25}$ pseudo-binary as a function of chromium concentration at 1,150 K

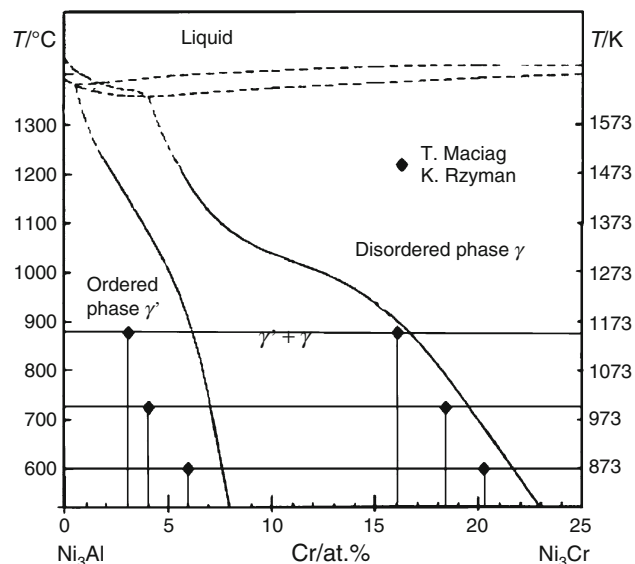


Fig. 8 Pseudo-binary system $\text{Ni}_{75}\text{Al}_{25}$ – $\text{Ni}_{75}\text{Cr}_{25}$ suggested by [7]. Points represent the locus of the phase boundaries obtained in the presented research

dissolving samples in bath as well as enthalpy of formation of alloys.

Results

Part of presented results was examined at 873 and at 1,150 K by one of the authors (K. R.) on previously designed calorimeter [9]. In studies mentioned above chromium concentration varied from 0 to 14 at.% and 0–25 at.%, respectively. It is worth mentioning that obtained results from [9] and from this work are very consistent.

Tables 1, 2, and 3 present values of enthalpy of formation obtained for alloys from range $\text{Ni}_{75}\text{Al}_{25}$ – $\text{Ni}_{75}\text{Cr}_{25}$ in three temperatures: 873, 996, and 1,150 K.

Discussion

In every temperature examined: 873, 996, and 1,150 K of $\text{Ni}_{75}\text{Al}_{25}$ – $\text{Ni}_{75}\text{Cr}_{25}$ pseudo-binary system, decrease of absolute values of enthalpy of formation $\Delta_f H$ is substantial with increase of chromium content in alloy. Figures 5, 6, and 7 present values of formation enthalpies as a function of Cr concentration for $\text{Ni}_{75}\text{Al}_{25}$ – $\text{Ni}_{75}\text{Cr}_{25}$ section at three examined temperatures.

All figures show characteristic points of break of $\Delta_f H$ course. They are attributed to location of phase boundaries $\gamma' / \gamma' + \gamma$ and $\gamma' + \gamma / \gamma$. This conclusion is due to the fact that the appearance of disordered γ phase with increase of chromium concentration causes more rapid decrease of absolute values of formation enthalpy. In

calorimetric solution method, it is connected with lower energy input necessary for bond breaking in dissolution process of γ than for γ' phase and is reflected by lower absolute values of formation enthalpy. Finishing of the appearance of disordered phase γ accompanies stabilization of formation enthalpy values which can be clearly seen in the all three figures.

Points obtained refer to places of existence of phase boundaries $\gamma' / \gamma' + \gamma / \gamma$ were placed on fragment of draft proposed by [7], it is shown on Fig. 8. Compositions of phase boundaries found in this work correspond to the lower chromium concentrations than these from [7]. The authors of this work consider that the difference is due to the fact that literature data are based on samples after quenching and while it was mentioned in [10, 11] that it is extremely difficult, often impossible to retain the structure of studied alloys by quenching. Very good compatibility of results obtained by authors on two independent devices is worth mentioning. In order to confirm the position of mentioned phase boundaries, authors are planning to continue calorimetric research and support it with another in situ method. In order to optimize course of phase boundaries $\gamma' / \gamma' + \gamma / \gamma$ in Ni–Al–Cr system results of formation enthalpy will also be applied in CALPHAD procedure.

Conclusions

1. A new high-temperature solution calorimeter was built, into which intermediate container with ten sockets is placed. It allows the direct determination of the formation enthalpy of alloys at elevated temperatures (up to 1,400 K).
2. The use of intermediate container makes it possible to heat the samples in order to achieve thermodynamic equilibrium. It also increases accuracy of results and shortens time of experiment thanks to using ten sockets.
3. Values of formation enthalpy of alloys from Ni₇₅Al₂₅–Ni₇₅Cr₂₅ pseudo-binary were determined at three temperatures: 873, 996, and 1,150 K with use “in situ” of calorimetric solution method.
4. With the increase of chromium content replacing aluminum in all three temperatures decrease of absolute values of formation enthalpy was found.
5. Based on significant breaks in the course of values of enthalpy as a function of Cr concentration authors claim that there are places of occurrence $\gamma' / \gamma' + \gamma$ and $\gamma' + \gamma / \gamma$ phase boundaries. This is a new possibility in calorimetric technique.
6. The authors conduct research with other “in situ” method (e.g., resistometry) to confirm rightness of this new way of determining the phase boundaries.
7. Obtained results will be used to develop the examined fragment of Ni–Al–Cr system with CALPHAD procedure.

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